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Water-Resistant Gypsum Binding Agents and Concretes Based Thereof as Promising Materials for Building Green

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Abstract. For gypsum-based cementing materials, environmental advantages are highlighted over Portland cement, and major method for increasing their water resistance are described. By the example of gypsum-lime slag binders, a successful application of water-resistant gypsums is demonstrated in the severe climatic conditions of the Ural region. Phase composition analysis results are presented for gypsum-lime slag stone-like material after years of operation as part of the concrete walls of enclosures. It is found that durability of the material can be explained by the formation of stable compounds: calcium sulfate dihydrate, calcium carbonates and calcium hydrosilicates of the type CSH(B).

1. Introduction

Under conditions of globalization, the continuous advance of science and technology raises environmental problems that become truly global in scale. It therefore appears both timely and necessary to spread impartial environmental information among public at large. This will promote to the modern society the principles of Sustainable Development, which has been officially assumed by the United Nations Organization to be a World Development Strategy. An integral part of the Sustainable Development is Building Green concept, which abates negative environmental impacts and complies with relevant ecology standards. The Building Green normally relies on the following most important criteria: effective use of natural resources; minimization of a construction project's negative impact on the environment in the processes of construction and further operation; creation of microclimate comfortable for humans; application of green structural materials that are environmentally assessed throughout their life-cycle and others.

Currently, truly green (ecologically clean) structural materials, such as wood and natural stone, have limited application, usually in residential building projects of individual housing construction. State-of-the-art industrial construction relies mostly on using artificial stone-like materials that may be attributed to different groups: one group may be called kilned materials (ceramics, glass) to be manufactured using high-temperature treatment; and the other group is non-kilned materials (concretes, mortars) to be formed using the process of solidification of binding agents. Among non-kilned composite materials, a leading position is taken by Portland cement, which is used mostly for making concrete and steel concrete. In terms of technical and economic characteristics, cement concrete represents a state-of-the-art structural material of widest application, which contributes significantly into creating material basis for human environment of modern civilization [1].

Non-kilned structural binding substance-based composites have certain advantages over natural and kilned stone-like materials: high manufacturability, economic efficiency, and a wide range of structural and technical performance characteristics. At the same time, these materials appear difficult for assessment in terms of their long-term behavior under specific operational conditions because they are characterized with prolonged processes of structure formation and may exhibit possible instability under the effect of external and internal factors. This concern is supported by a number of publications devoted to the issues of the materials durability and safety in operation. Many authors have reported about higher rates of corrosion processes in structures made of steel concretes, which become considerably costlier for repair and reconstruction. More frequent occurrences of construction accidents are observed involving sudden collapse of concrete structures, which as a rule date no more than 30–40 years back [2–4]. Although Portland cement has a long history of use nearly as long as 200 years, there are still unceasing discussions going on over the "driving force" of hydration processes in clinker minerals, over the roles played by surface phenomena occurring on the cement grain/water interface, and over internal structural strains that inevitably result in the drop of strength and in cyclic "saw-like" solidification behavior of cement stone [5].

Environmental compatibility of cement concretes also demands serious scrutiny, considering the resource-intensive and environmentally hazardous technology applied for manufacturing Portland cement, which reportedly produces 5 % of CO_2 emissions globally. These issues cause serious concern over the prospects for cement industry development; active search for alternative technologies is thus initiated; and synthesis research is intensified in creating and investigating alternative low-clinker, geopolymeric, gypsum-based water-resistant materials and other binder systems [6, 7].

2. Characterizing gypsum-based binding agents and methods for increasing their water resistance

Gypsum-based binding agents represent a kind of very few synthetic structural materials that can indeed be regarded eco-friendly. Raw materials used for making such binders are sedimentary rocks containing calcium sulfate dihydrate; possibly, as starting materials can also be used the chemical industrial wastes, such as phosphogypsum, borogypsum, fluorogypsum. The annealing temperature for the prepared starting material does not exceed 150–200 °C (compare with the annealing temperature for Portland cement at 1,500 °C), and the corresponding reaction byproduct is water:

$$CaSO4 \cdot 2H2O = CaSO4 \cdot 0.5H2O + 1.5H2O \tag{1}$$

When thus obtained gypsum-based binder is mixed with water, a spontaneous hydration reaction runs intensely, i.e., the reverse reaction occurs:

$$CaSO4 \cdot 0,5H2O + 1.5H2O = CaSO4 \cdot 2H2O \tag{2}$$

Hydration is a complicated physicochemical process that involves dissolving calcium sulfate hemihydrate, creating nucleation centers for solidification of a new phase, growing the nuclei and crystallization of calcium sulfate dihydrate. As the gypsum crystallites grow and interweave, the polycrystalline internal structure of synthetic stone is formed, with its macroscopic structure featured with high porosity (25–40 %) because of the great (up to 70 %) water consumption at the stage of mixing with water. Therefore, thus solidified gypsum binder is characterized with a high absorption of water and a low softening coefficient: in the water-saturated condition the strength of synthetic gypsum-based stone decreases by 40–50 %. Gypsum-based structures exhibit considerable creep under humidification and show low resistance to weather and, being such, are not to be recommended for operation in weather conditions.

A universal method for increasing water and weather resistance of non-kilned structural composite materials is decreasing their porosity. To this end, binder systems are introduced with small amounts of polymeric or plastizing additives to increase their density. For binder systems non-resistant to water, which include gypsum-based binders, a more drastic way of increasing weather resistance is to add up to 10–40 % of mineral components that, due to their intrinsic binding properties, solidify into

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water-resistant synthetic stone-like material. Such components are referred to as “hydraulic” components and thus produced binders are often called “mixed gypsums”. There are two major directions known in the world to have been formed in the practical approach to solving the issue of increasing water-resistance of gypsum-based binders: one direction has been reported [8–10] to be aimed at using some amount of Portland cement as a hydraulic component; and the other direction [11–13] is to develop cement-free compositions based on lime and active mineral supplements.

It should be noted that the processes of hydration in mixed gypsum binders have thus far received insufficient research coverage. Under certain conditions, there is a danger of forming destructive phases (such as ettringite, thaumasite), which may result in increasing volume, cracking development and destruction of the solidified synthetic stone [14]. Such risks appear to be the reasons for insufficient use of water-resistant gypsum-based binders in construction, despite a multiple body of laboratory investigations and research publications available.

3. Industrial experience in manufacturing water-resistant gypsum-lime slag binders and concretes in the Ural Regionother section of your paper

In Russia, among water-resistant gypsum-based binders, most known are multi-component gypsum cementitious pozzolanic binders (GCPB) and gypsum-lime slag binders (GLSB), developed in the last century. Authorship rights for these binder systems are known to belong to Russian Institutions of Higher Learning: GCPB was developed in the Moscow Institute of Construction Engineering (now S.M. Kuibyshev’s Moscow State Construction University); and GLSB system was developed in the Ural Polytechnical Institute (now B.N. Yeltsyn’s Ural Federal University). The Moscow school of thought in science and engineering (A.F. Volzhensky, A.V. Ferronskaya, A.F. Korovyakov, et al) suggested using Portland cement and active mineral supplements (pozzolans) as the hydraulic component in the mixed gypsum-based binders. The scientists from the Ural Federal University (A.A. Antipin, L.I. Ryabokon, S.V. Bednyagin, et al) directed their attention to creating water-resistant gypsum-based compositions through the use of alkali and sulfate activation of blast-furnace acidic slags avoiding the use of cement.

In 1952, in the Ural Polytechnical Institute, a Gypsum Concrete Laboratory was established under the direction of A.A. Antipin, which developed GLSB compositions and studied GLSB properties, with further implementation of the developments into industrial technologies for manufacturing light concretes (GLSB concretes). At different stages of the lab’s scientific activity, a number of various teaoms were involved in joint efforts: the teams included scientists, faculty members and students from eight departments of the Ural Polytechnical Institute and Sverdlovsk Architectural Institute; there were also members from medical sanitarian staff and from the staff of the specialized design and scientific research organization of the Sverdlovsk region, Ufa, Moscow and Moscow region [15]. Three experimental industrial plants were designed, which had over the period from 1960 to 1972 been used to manufacture GLSBs and GLSB-based wall blocks and sanitary units. The manufactured products were used to build over a hundred of experimental structures of various purposes: one and two-story residential houses, administration buildings, manufacturing facilities, agricultural buildings and structures. Monitoring the construction projects and laboratory tests have proved that increasing water-resistance of GLSB concrete as compared to commonly used gypsum concrete manifests itself not so much in increasing softening coefficient as in a considerable, over two orders of magnitude, decrease in the parameters of creep. The results were used as a basis for designing and constructing the-first-in-the-country gypsum works to manufacture GLSB blocks, with no similar works known abroad. The gypsum works was established in Krasnoufimsk, Sverdlovsk region, in 1976. The major gypsum concrete products were large-size wall blocks of 400 mm in unified thickness, 800 to 3,600 mm in length, and 800 to 1,600 mm in height. Thousands of buildings were constructed using the manufactured blocks: residential houses of various purposes, schools, kindergarten facilities, drug-stores, cattle-breeding facilities, fertilizer stores, granaries, garages, agricultural machinery service shops, etc. The gypsum works stopped producing GLSB concretes in the 1990s as construction business experienced a slump in building volume.

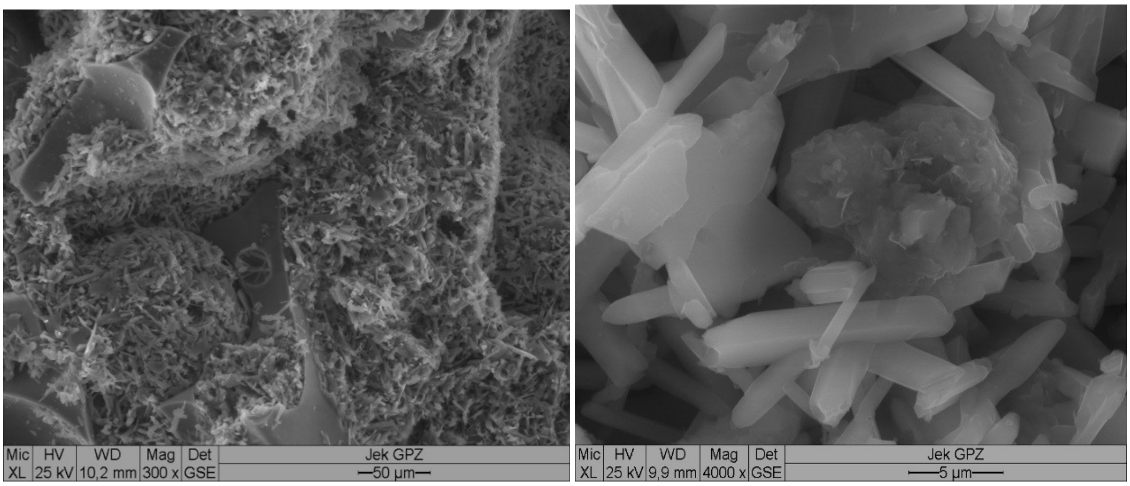
For ten buildings erected in 1965–1985 of GLSB concretes on the territory of Sverdlovsk region, scientists from the Ural Federal University some years ago carried out a checkup which demonstrated that the buildings have remained in good condition and showed no sign of decay. The analysis results of the physical and mechanical properties of the wall structures have showed not only a high weather resistance of GLSB concrete but have also demonstrated considerable hardening of the material. At a density ranging between 1,200–1,700 kg/m^3 (depending on the type of filling) and at a designed strength of 5–10 MPa, the actual strength of the concrete was found to be 10–15 MPa [12].

4. Features of structure formation of gypsum-lime slag binders

The mechanisms underlying solidification of water-resistant gypsum-based binders is a complicated physicochemical process covering, on the one hand, hydration and crystallization of sulfate compounds to produce calcium sulfate dihydrate, and, on the other hand, formation of water-resistant crystalline and/or gel-like phases, such as calcium hydrosilicates and hydroaluminates running at the expense of reactions between the components of the hydraulic supplement. For GLSB concrete produced at the Krasnoufimsk gypsum works, such components were blast-furnace ground granulated slag having a basicity factor not exceeding 1 and burnt and ground lime.

To explore the features characterizing the prolonged structure formation of GLSB, the present study reports about studies carried out on small fragments of concrete taken from external uncovered surfaces of wall structures built in 1973 in Patrushi, Sverdlovsk region. Physical and chemical studies carried out on the selected samples were performed at the Laboratory of Structural Analysis Methods and Properties of Materials and Nanomaterials at the Ural Federal University, with some of the tests carried out at the Electron Microscopy Laboratory of the Bauhaus University (Weimar, Germany).

It is found that synthetic stone based on GLSB prolonged solidification is a rather dense and uniform structure comprising impregnated grains of slag (Figure 1, a). At a large magnification, it can be seen that the phase composition of stone material contains both well-crystallized structures and fragments of gel-like formations (Figure 1, b).



a b

Figure 1. Microstructure of GLSB after long years of hardening

X-ray phase analysis showed that the major crystalline phase identified with the reflections: 7.58; 4.26; 3.78; 3.05; 2.86; 2.67; 2.21; 2.07; 1.89; 1.62 is calcium sulfate dihydrate. It is likely that there is also low-base calcium hydrosilicates (3.04; 2.84; 1.88) and secondary calcium carbonate, which reflections are overlapped with the hydrate phases reflections (3.02, 2.27, 2.08, 1.87).

The presence of hydrosilicate and calcium carbonates in the composition of synthetic stone is supported with the results of differential thermal analysis. Endothermal effect at 160 °C confirms removal of chemically combined water from the hydration products of gypsum part of the binder; and exothermal effect at 369 °C is associated with the polymorphous transformation of dehydrated sulfate phases; the blurred endothermal effect in the range of 700–750 °C is due to the processes of decarbonizing of the secondary calcium carbonate formed as a result of lime carbonization in GLSB.

In the same temperature range, there seems to be dehydration of low-base crystalline and gel-like calcium hydrosilicates produced as a result of pozzolanic reactions between fine-grained slag component of GLSB and lime. In our opinion, it is crystallization of dehydrated hydrosilicates that may be associated with the exothermal effect observed in the temperature range of 830–860 ºC. From the temperature of phase transformation, the basicity of calcium hydrosilicates of CSH(B), which were fromed as part of GLSB composition, can be assumed to be equal to 1.36 ($CaO/SiO_2 = 1.36$) [16].

For the formation of calcium hydrosilicates as part of the mixed gypsum composition, the source of silicon oxide is ground granulated blast-furnace slag. Our investigations have shown that dissolving of the slag surface in the GSLB composition occurs non-uniformly (Figure 2).

Figure 2. Particle of granulated blast furnace slag covered with products of pozzolanic reactions

The fragmentariness revealed in the "erosion" pattern of a slag particle, which is the source of silicate component for pozzolanic reactions, confirms the presence of microgranularity observed for the vitreous phase of granulated blast-furnace slags and supports the toponymic mechanism underlying the formation of calcium hydrosilicates [17].

Therefore, hardening of GLSB concretes revealed upon decades of their operation as part of the external wall structures has objective reasons and can be explained by slow processes of interaction between the vitreous phase of sag and calcium hydroxide resulting in the formation of both gel-like and crystalline calcium hydrosilicates.

5. Conclusions

Water-resistant gypsum-based binders can by no means be regarded as a fully adequate replacement for Portland cement; however, they meet the Building Green requirements for structural materials and show promise for low building structural applications. Successful production and application of GSLB for making concrete wall structures in the Urals in the 1960–1980s is a good evidence to that. After nearly fifty years of use in rather severe climatic conditions, the materials have revealed not only the absence of any signs of deterioration but even exhibited a 1.5–2.0 time increase in their structural strength. According to our studies, the reason for that is the stable phase composition of the synthetic gypsum-lime slag stone-like material without any destructive compounds. Along with well-crystallized calcium sulfate dehydrate, the material also contains some quantity of carbonate compounds and calcium hydrosilicates having both crystalline structure of CSH(B) type, with the basicity presumably equal to 1.36.

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